KINETIC ANALYSIS OF DSC AND THERMOGRAVIMETRIC DATA ON COMBUSTION OF LIGNITE

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Abstract

Thermal analysis increasingly being used to obtain kinetic data relating to sample decomposition. This work involves a comparative study of several methods used to analyse DSC and TG/DTG data obtained on the oxidation of Beypazari lignite. A general computer program was developed and the methods are compared with regard to their accuracy and the ease of interpretation of the kinetics of thermal decomposition. For this study, the ratio method was regarded as the preferred method, because it permits the estimation of reaction order, activation energy and Arrhenius constant simultaneously from a single experiment.

Keywords: activation energy, combustion, differential scanning calorimetry, kinetics, lignite, oxidation, thermogravimetric analysis

Introduction

Thermal analysis is defined by the International Confederation for Thermal Analysis as including all techniques with which the change in a physical property of a substance and/or of its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program.

Non-isothermal methods of determining reaction kinetics continue to be studied. During recent years, several methods have been developed to allow the kinetic analysis of TG and DSC data, but few attempts have been made to compare them critically. Kinetic parameters for the thermal degradation of solids have been determined from thermogravimetric data obtained at single heating rates in a number of studies [1, 2].

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Friedman [3] recently performed kinetic calculations based on measurements made at four different heating rates. This method makes use of the fact that the TG curves are shifted to higher temperatures with increasing rates. Michelson and Einhorn [4] compared three different methods with regard to their accuracy and the ease of interpreting the kinetics of thermal decomposition. Dollimore and Heal [5] demonstrated that non-isothermal traces of thermal decompositions of solids must fit the equation developed by Freeman and Carroll [6] for the kinetic analysis of 'n-order' reactions, even if they follow a quite different mechanism. Flynn [7] developed a general differential method in which the activation energy and pre-exponential factor are determined as functions of the degree of conversion from sets of two or more experiments with different thermal programs. Chen et al. [8] developed computer programs to evaluate kinetic analysis findings from non-isothermal thermogravimetric data based on single and multi-heating rate procedures. The single heating methods include the differential and integral calculations, while the multi-heating rate methods include those of Friedman approximation. Zsakó et al. [9] developed computer programs for three integral methods of deriving kinetic parameters from TG curves. The first method is a computerized variant of Doyle's [10] curve-fitting method and performs the calculation of the exponential integral by means of the author's empirical formula. The other two methods are variants of the Coats-Redfern [11] linearization method. Testing of the methods on both theoretical and experimental TG curves shows them to be almost equivalent. Šesták [12] compared the kinetic results calculated by five different methods. From these calculations, it was found that the deviations of the computed values of activation energy did not differ by more than 10%. Thus, all the methods appear to be satisfactory for the calculation of activation energy within the limits of accuracy required.

A method which measured the heat evolution of solutions and solids by DSC was first described by Borchardt and Daniels [13]. Rate constants and activation energies are calculated from the analysis of DSC curves. Hugo et al. [14] presented a new evaluation method for determining the kinetic parameters of a chemical reaction from DSC measurements. This method evaluates a series of DSC curves at different heating rates. The activation energy, the pre-exponential factor and a general description of the concentration dependence of the reaction rate are obtained.

Yang and Steinberg [15] proposed a model for determining the kinetic parameters from a single DTA curve for a general n^{th}-order reaction. Liu et al. [6] modified the Yang and Steinberg model and obtained a fairly convenient one. However, both methods are still complicated and have to be solved by a trial and error approach. Blecic et al. [17] introduced the least squares method to calculate the kinetic parameters from a single DTA curve. However, the validity of this method is limited to values of E/RT less than unity.

In the present work, the thermal decomposition of Beypazari lignite was studied by using DSC and TG/DTG techniques; kinetic parameters were estimated and compared by means of eight different methods.

Experimental

The sample studied was Beypazari lignite (Table 1), ground to a particle size of <60 mesh and prepared according to ASTM standards. It is believed that for such a small particle size the effect of temperature distribution within the sample particles is eliminated. In order to obtain a homogeneous structure throughout the experiments, the lignite sample was dried in an oven at 110°C for 2 h.

Table 1 Properties of Beypazari lignite

Proximate analysis	
Moisture/%	8.60
Volatile matter/%	29.95
Ash/%	36.40
Fixed carbon/%	25.05
Calorific value/kJ mol^{-1}	16135
Ultimate analysis	
Carbon/%	37.95
Hydrogen/%	2.90
Nitrogen/%	1.40
Oxygen/%	7.66
Sulphur/%	4.79

All the experiments were performed with DSC and TG/DTG equipment attached to the DuPont 9900 thermal analysis system. Thermal experiments were conducted with a sample size of 10 mg in the temperature range 20–700°C. The gas flow rate which supplied excess oxygen during the experiments was kept constant at 53 ml min^{-1}. The constant heating rate for TG analysis was 10°C min^{-1}. For determination of the kinetic parameters of the sample by means of the ASTM method, experiments were performed at 5 different heating rates (5, 10, 15, 20 and 25°C min^{-1}), and for reproducibility each experiment was repeated twice.

The DSC equipment was calibrated for temperature readings by using indium as standard for reference. In this calibration, indium was heated from ambient temperature to 175°C at five different heating rates and the necessary temperature corrections were made. The TG/DTG system for temperature read-
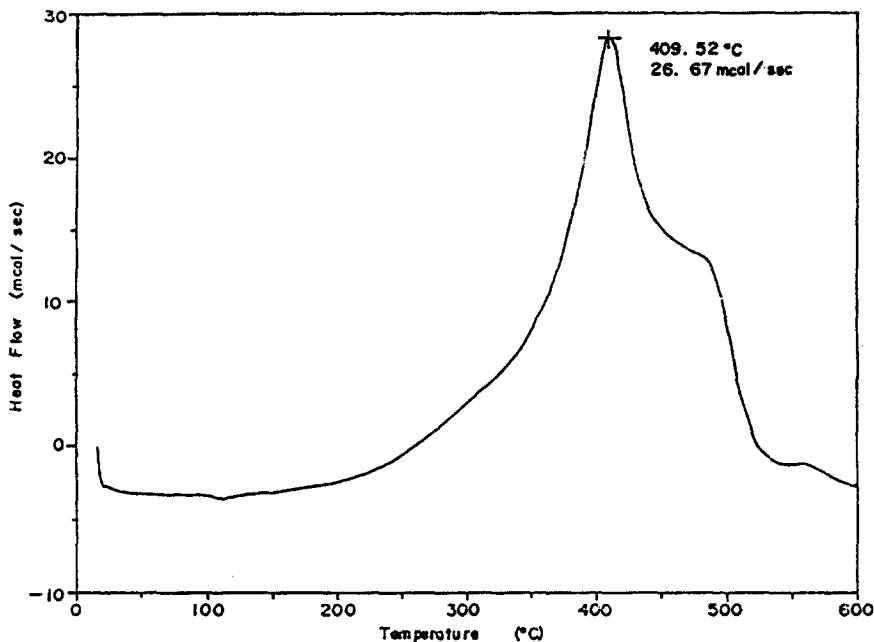
Fig. 1 DSC curve of Beypazari lignite

ings was calibrated with calcium oxalate monohydrate. Before the TG/DTG equipment could be used for quantitative estimation of mass changes during combustion experiments. It was essential to calibrate the balance for buoyancy effects up to 700°C. The material chosen for this purpose was silver, which has a melting point of 960.8°C. A run using silver was performed at a heating rate of 10°C min^{-1} and the apparent mass changes were recorded as a function of temperature. DSC and TG/DTG curves obtained during the combustion of Beypazari lignite are presented in Figs 1, 2 and 3.

Methods used for kinetic analysis

The calculation of kinetic data is based on the formal kinetic equation

$$d\alpha/dt = k\alpha^n$$

where α is the amount of sample undergoing reaction, n is the order of reaction and k is the specific rate constant. The temperature dependence of k is expressed by the Arrhenius equation:

$$k = A \exp(-E/RT)$$

where A is the Arrhenius constant, E is the activation energy and R is the gas low constant.
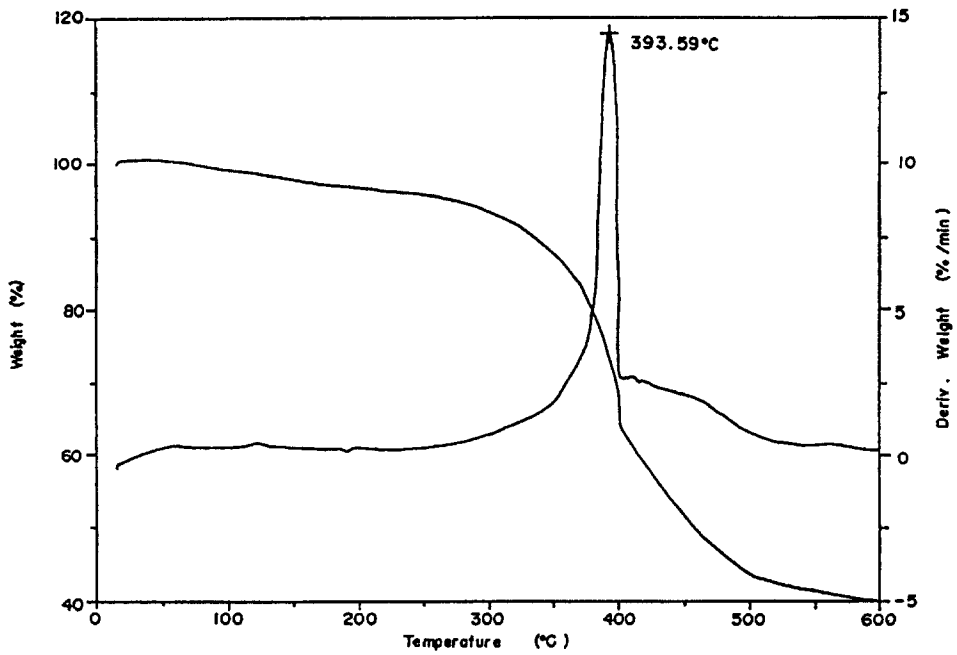
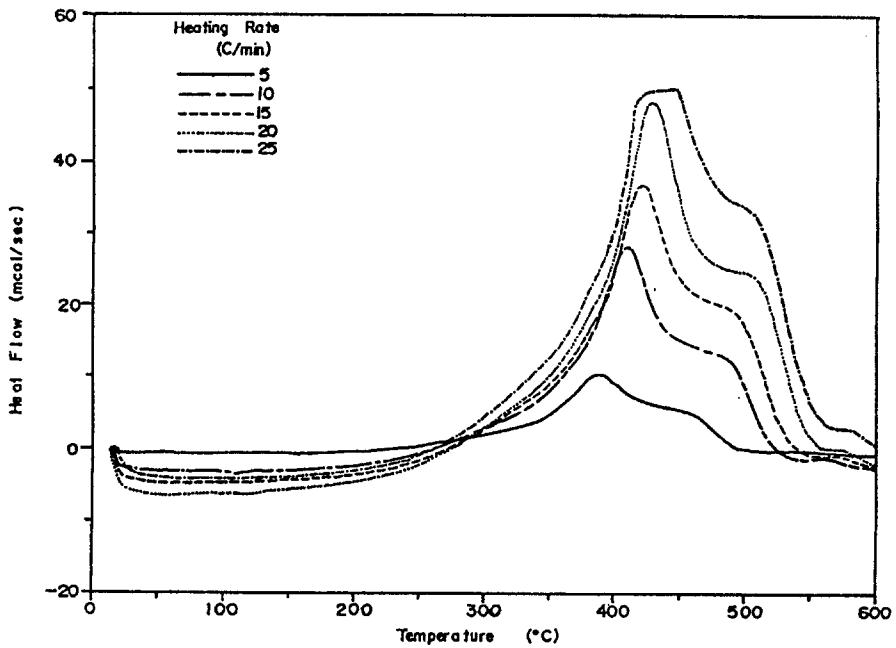**Fig. 2** TG/DTG curve of Beypazari lignite

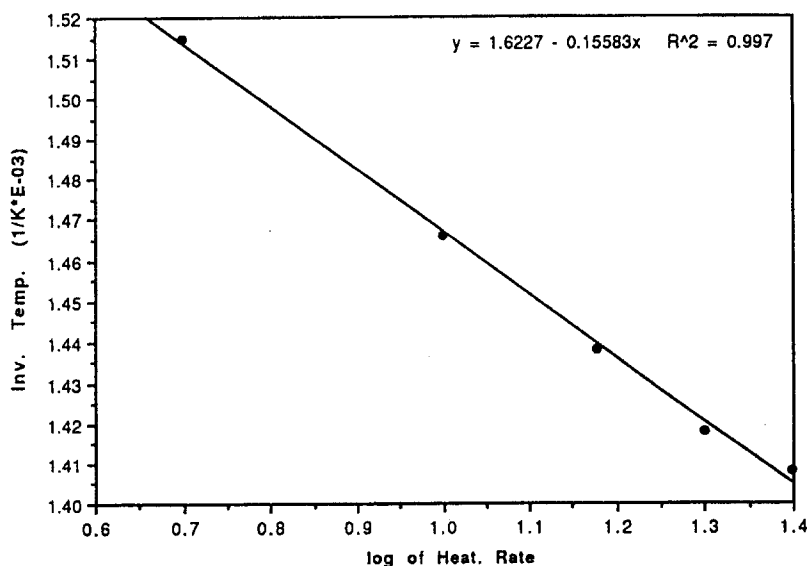**Fig. 3** DSC curves of Beypazari lignite at different heating rates

Fig. 4 Inv. temp. *vs.* log of heating rate (ASTM-1)

Methods for analysing DSC data

ASTM method 1 [18]

In this method, the sample temperature is increased at linear heating rates (5, 10, 15, 20 or 25°C min^{-1}) and any exothermic peaks are recorded (Fig. 3). The reciprocals of the temperatures at which the reaction peak maxima occur are plotted as a function of the log of the respective heating rates (Fig. 4). In this method, a trial and error procedure is used and the activation energy is calculated from the slope as follows;

$$E = -2.19R\{d \log_{10}\beta/d(1/T)\}$$

where β is the heating rate.

ASTM method 2 [18]

An alternative method for calculating activation energies according to ASTM standards is also proposed. In this method, $-\ln(\beta/T^2)$ is plotted *vs.* $1/T$ and the activation energy is calculated from the slope as follows:

$$E = \{R \, d[-\ln(\beta/T^2)]\}/d(1/T)$$

Roger and Morris method [19]

A kinetic model developed by Roger and Morris gives a means of estimating activation energies from DSC curves. The recorded DSC data are in the form of distances between the curve and the baseline at the associated absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$-E = R \{(\ln D_1 - \ln D_2)/(1/T_1 - 1/T_2)\}$$

where D_1 and D_2 are two distances from the baseline at the associated temperatures T_1 and T_2. The effect of the heating rate on the kinetic parameters of the samples studied was also investigated [20] and the results are given in Table 2.

Table 2 Peak temperature and activation energies of Beypazari lignite from DSC data at different heating rates using Roger & Morris method [19]

Heating rate/°C min^{-1}	T_{peak}/°C	E/kJ mol^{-1}
5	387	63
10	409	69
15	422	66
20	432	69
25	437	65

Methods for analysing TG/DTG data

n=1 method [21–23]

In this method, since the measured rate of mass loss accounts for gross changes in the system, the Arrhenius-type reaction model assumes that the rate of mass loss of the total sample is dependent only on the rate constant, the mass of sample remaining (w) and the temperature. The final form of the equation is as follows:

$$\log\{(dw/dt)/w\} = \log A - E/2.303RT$$

In the plot of $\log\{(dw/dt)/w\}$ *vs.* $1/T$, there appear to be regions of marked linearity. The slope of such a linear portion is proportional to the activation energy, and the intercept to the Arrhenius constant (Fig. 5).

Coats and Redfern method [11]

Coats and Redfern developed an integral method which can be applied to TG/DTG data, assuming the order of the reactions. The correct order is pre-
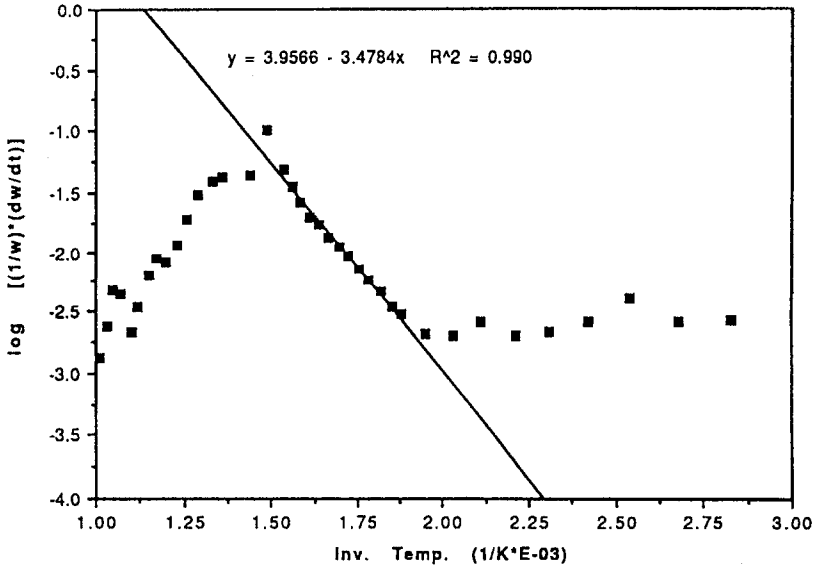
Fig. 5 Arrhenius diagram of Beypazari lignite ($n=1$ method)

sumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation which is used for analysis is

$$\log\{1-(1-\alpha)^{1-n}/T^2(1-n)\} = \log\{(AR/\beta E)(1-2RT/E)-(E/2.303RT)\}$$

where β is the linear heating rate. Thus, a plot of $\log\{1-(1-\alpha)^{1-n}/T^2(1-n)\}$ vs. $1/T$ should result in a straight line of slope $= -E/2.303R$ for the correct value of reaction order (Fig. 6). In this study, the reaction order was assumed to be 1/2, 2/3, 1, 3/2 or 2. The activation energies obtained with these reaction orders are given in Table 3. It was concluded that the reaction order was between 2/3 and 1.

Ratio method [24]

This method, which was based on the Arrhenius kinetic model, was developed by Michelson and Einhorn. The kinetic model assumed in this method is of the form

$$(-dw/dt) = A \exp(-E/RT)w^n$$

The form of the equation used to estimate kinetic parameters is

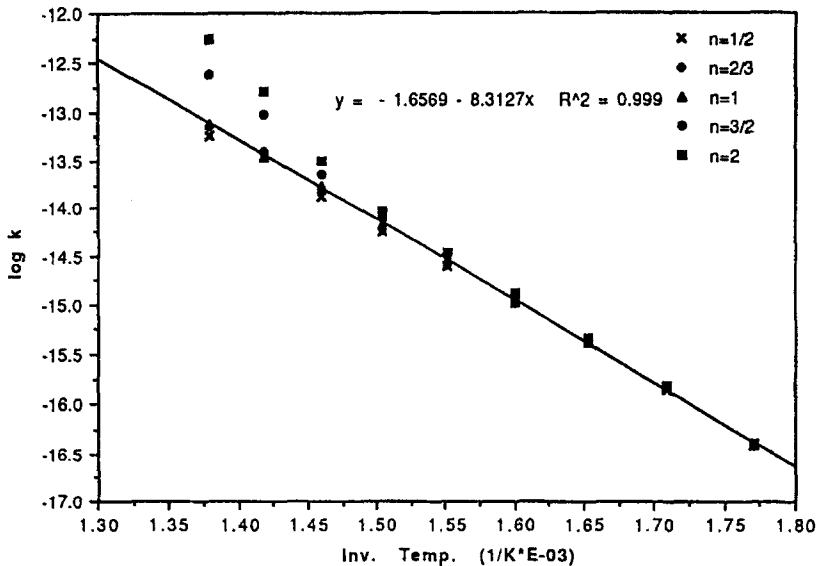$$\log\{(-dw/dt)_j/(-dw/dt)_i\} = E/2.303R\{(T_j-T_i)/T_iT_j\}\log(w_i/w_j)^n$$

Fig. 6 Arrhenius diagram of Beypazari lignite (C&R method)

Table 3 Activation energy from Coats & Redfern [11] method using TG/DTG data

Reaction order	E/kJ mol^{-1}	Corr. coeff.
1/2	68	0.996
2/3	72	0.997
1	76	0.999
3/2	85	0.995
2	96	0.987

In the plot of $\log\{(-dw/dt)_i/(-dw/dt)_j\}$ vs. $\{(T_j-T_i)/(T_iT_j)\}\log(w_i/w_j)^n$, there appear to be regions of linearity with slope $= -E/2.303R$ and intercept $=n$. In this method, the ratio must be chosen to be near unity to yield enough data points for determination of a reliable correlation covering the desired portions of the DSC curves. In this study, TG/DTG curves were analysed for a selected ratio of 1.1.

Maximum point method [24]

The TG/DTG curves of the samples show that the rate of decomposition has a maximum and the kinetic parameters can be determined from the point at which this maximum occurs. The calculations involved in determining the kinetic parameters are simple to perform. The following relationship was used to determine the activation energy and Arrhenius constant:

$$E = RT^2/\{w(-dw/dT)\}$$

$$A = (\beta E/RT^2)\exp(E/RT)$$

where β is the heating rate, w is the fraction of material remaining at the maximum rate of mass loss and T is the absolute temperature at the maximum rate of mass loss. Since the calculations are simple, many thermoanalytical curves may be examined in a short time. The major disadvantage of this method is that the kinetic parameters are determined from a single point in the thermoanalytical curves, which means that the researcher must accept the power-model equation blindly.

Ingraham and Marier method [25]

Ingraham and Marier developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. The rate constant may be expressed as $k=dw/dt$ where dw represents the loss in mass from unit area in the period of time dt. The temperature at any time is $T=b+\beta t$, where β is the heating rate and b is the initial temperature. They showed that, if dt is replaced by dT/a, then

$$\log(dw/dT) = \log T - \log\beta + \log A - E/2.303RT$$

The activation energy is calculable from the slope of the plot $[\log(dw/dT)-\log T+\log\beta]$ *vs.* $1/T$.

Discussion and comparison of methods

The non-isothermal kinetic study of mass loss during a combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions. Five different methods, all based on the Arrhenius kinetic theory, were used for the kinetic analysis of the TG/DTG data and three different methods were used to determine the kinetic parameters from the DSC data. In all these methods, calculations were performed to estimate the kinetic parameters as activation energy, Arrhenius constant and reaction order. The computer programs written allow the kinetic parameters to be determined by regression analysis, the slope and intercept of a straight line being calculated by curve fitting.

Analysis of DSC data

The two methods called ASTM methods, used to evaluate DSC data for the estimation of kinetic parameters, assume that $n=1$ and involve a similar kinetic

model that includes the heating rate. The calculated activation energies were therefore similar (Table 4).

Table 4 Comparison of kinetic data obtained using different methods

Method	$E/\text{kJ mol}^{-1}$	Arrh. const./1 min^{-1}	Reaction order
$n = 1$	66.0	1.2E+04	1.0
Coats & Redfern	76.0	2.8E+04	1.0
Ratio	63.0	1.0E+04	1.09
Max. Point	84.5	2.8E+06	1.0
Ingra. & Marrier	82.0	2.6E+06	1.0
ASTM-1	66.0	1.4E+04	1.0
ASTM-2	66.0	1.4E+04	1.0
Roger & Morris	69.0	3.4E+04	1.0

The Roger and Morris [19] method utilizes the distance from the baseline to the DSC curve at points below the decomposition temperature. The effect of the heating rate on the activation energy E is given in Table 2: E was in the range 63–69 kJ mol^{-1} [20].

Analysis of TG/DTG data

The method were $n = 1$ was assumed a priori for the calculations permits estimations of the activation energy and Arrhenius constant from the linear plot of $\log\{(dw/dt)/w\}$ vs. $1/T$ (Fig. 5).

The Coats and Redfern [11] method involves a trial and error procedure, where the reaction order is estimated until the best straight line is obtained from $\log\{1-(1-\alpha)^{1-n}/T^2(1-n)$ vs. $1/T$ plots. The activation energy and Arrhenius constant are then calculated from the slope and intercept, respectively (Table 3).

In the maximum point method, only the peak temperature as recorded in the DTG curve and the derivative of the TG curve with respect to temperature at that maximum point are used for estimation of the activation energy and Arrhenius constant. Since a single point is used for evaluation, it is not expected that representative values are possible. This can also be seen in Table 4; the maximum activation energy was estimated with this method.

In the Ingraham and Marier [25] method, the estimation procedure incorporates the rate sample heating during the test. This method also assumes a unit reaction order. The activation energy value estimated is one of the highest (Table 4).

In the ratio method [20], the reaction order and activation energy are estimated from the slope and intercept of the straight line portion of the

$\log\{(-dw/dt)_j(-dw/dt)_i\}$ vs. $\{(T_j-T_i)/(T_iT_j)\}\log(w_i/w_j)^n$ curve. The method involves a critical step of selecting the best ratio for T_j and T_i and corresponding $(-dw/dt)_j(-dw/dt)_i$ values. A ratio that gives a large number of data in the reaction interval gives a better-defined straight line. Table 4 shows that the reaction order for lignite oxidation is 1.09. With this method, it was possible to justify why $n=1$ as assumed in the above methods was an acceptable assumption.

In this work, the ratio method was the preferred method because it enabled us to estimate reaction order, activation energy and Arrhenius constant simultaneously from the experimental data.

Conclusions

This work compared eight different analysis procedures proposed in the literature, i.e. five methods for TG/DTG data and three methods for DSC data, for solid fossil fuel oxidation.

The Beypazari lignite sample used in this research had a calorific value of 16135 kJ mol^{-1}, a 36.4% ash content and an 8.6% moisture content.

The heating rate during the experiments was 10°C min^{-1}; only the ASTM methods for DSC analysis necessitated data obtained at different heating rates.

The reaction order as estimated from the ratio method for lignite oxidation is unity. The activation energy was 63 kJ mol^{-1} and the Arrhenius constant $1.0\,E+0.4$ min^{-1} under the test conditions applied.

Of all the methods studied, the ratio method was preferred because it was possible to estimate reaction order, activation energy and Arrhenius constant simultaneously from a single experiment.

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